A NOTE ON THE SLUDGE FORMATION OF THE TAN LIQUORS IN THE TAN YARD*

D. GHOSH, K.R.V. THAMPURAN, AND M. BALAKRISHNAN

Central Leather Research Institute, Madras

The Indian leather manufacturers use mainly aqueous extracts of babul and myrab for the manufacture of heavy leathers. Some tanners also use water extract of mangrove bark and wattle extract along with these two tanning materials. During tannage, plently of sludge is accumulated in the tan pits, which are mainly from myrab liquors and partly from other liquors. It was reported ^{1,2} that the aqueous extracts of myrab and babul lose plenty of tanning in the form of sludge, when these are exposed to air. In the case of myrab, some of the components namely chebulinic acid and ellagic acid go out of the solution after a few days of extraction and settle at the bottom of the tan pit in the form of sludge. Moreover, part of gallic acid which is slightly soluble in water, is likely to be shifted out of the colloidal solution and settle with the previous two components. Highly polymerised tan molecules of condenced tanning materials likewise settle at the bottom of the pits in the form of sludge, after they exceed their critical limit.

The present experiment was undertaken to show the difference between the sludge formation in the tan pits containing blended liquors of hydrolysable and condensed tanning materials with and without pelt pieces.

Experimental

- (a) 3 Kg. each of crushed babul and mangrove barks were blended separately with one Kg. of crushed myrab nuts, and 4 times of water were given in each case. These were then kept for 18 hours and then filtered. One litre from each was kept as blank and in another litre, in each case, delimed pelt weighing 100 gms was put. The blanks and the liquors with the pelts were then kept in this condition for 15 days, after which the pelt pieces were taken out and washed. Sludge formation in all the cases was then determined after centrifuging the liquors and drying under vacuum. The result are given in the Table I.
- (b) 300 gms each of crushed babul and mangrove bark were blended separately with 100 gm. of myrab in two beakers and 1600 ml. of water was added in each (2 Nos.) were taken seperately in 4 beakers. 4 times of water was then added in each case. All these were kept in this condition for 18 hours and then filtered through cloth. Separately leached liquors of myrab, were than mixed with the liquors of babul and mangrove. The Barkometer strength and total volume of all the liquors were then noted. 4 pieces of delimed pelt were then put in the liquors maintaining the pelt/liquor ratio as 1:10. The pieces were then kept in the liquors for 15 days, after which the sludge formation was deter-

3

TABLE—I
Sludge Formation in the Blended Liquors With and Without Pelts

Experiment No.	Nature of blend (in quantity)	Volume of liquor	° <i>BK</i>	Sludge litre (gm.)
1.	Mangrove—3	1 litre	18	With pelt—7.
	Myrab—1			Without pelt—6.7
2.	Babul—3	1 litre	18	With pelt—5.6
	Myrab—1			Without pelt—4.7

mined after centrifuging the liquors and drying the sludge in the vacuum pan to a constant wt. The results are given in the Tahle II.

TABLE—II

Sludge Formation in the Used Liquors, (after tanning pelts).

Experiment No.	Nature of blend (in quantity)	Volume of liquor collected	°BK	Wt. of sludge in gm.	Sludge/litre (gm.)
1.	Mangrove—3 + Myrab—1	1050	18	7.25	6.9
2.	Babul—3 + Myrab—1	880	18	4.8	5.4
3.	Mangrove (3) and myrab (Separately leached and blended	1080	18	6.1	5.6
4.	Babul (3) and Myrab (1) Separately leached and blended	900	18	4.6	5.1

Discussion of Results

From the resuls, it was observed that the sludge formation of both the blended liquors (babul+myrab and mangrove+myrab) used for tanning pelts, was slightly more than the liquors which were kept as blank: the blended liquors of mangrove and myrab showed more of sludge formation than those of babul and myrab.

Presumably, when the liquors were extracted from the blended tanning materials some components which are otherwise insoluble are extracted because of mutual solubilisation effect³ and held in suspension by the solubilised tan molecules. But the equilibrium of the liquor is likely to get disturbed when the tan molecules responsible for keeping some of the components in suspension, penetrate through the pelts; with the result, the suspended components presumably precipitate in the form of sludge. This might explain more of sludge formation in the liquors where pelts are tanned. The experiment thus showed that the conception, that the peptised molecules penetrate through the pelt along with their carriers and act as fixed tans, may be fallacious.

In the case of mangrove tannis, which are mainly based on leucocyanidin^{4.5} and which contain comparatively higher particle size as compared to babul are likely to get polymerised quickly during tanning and a part of it precipitates in the form of sludge when these exceed their critical limit. Those precipitated molecules are likely to weigh more than those of babul molecules. This would presumably suggest more yield of sludge in the mangrove-myrab liquor.

Sludge formation was found to be more in the used liquor (in which pelt was tanned) derived from the blended materials prior to leaching as compared to that made up with liquors, leached separately and then blended. The sludge formation in the case of babul and myrab blends, however, did not show much difference in both the cases. The penetration of both the liquors through the pelts was found to be almost the same.

The yield of sludge in both the cases of the blends of babul and myrab was found to be much less as compared to those of mangrove and myrab. One reasonable explanation might be that the volume collected in the case the blends of babul and myrab are much less than those of mangrove and myrab and consequently the difference in the sludge formation. Other probable reasons have already been explained before.

This experiment thus showed that if the hydrolysable and condensed tanning materials are first blended prior to leaching and then the leach liquor is used for tanning, the sludge formation in the tan pits is not minimised, rather it is increased in some cases. It was suggested that the different types of tanning material could only be blended the leached when the solubility and tan content of the materials are almost the same or differ only slightly. Otherwise, the one which is

more soluble in water is extracted first thereby decreasing considerably the solubility of the tannins of other tanning materials. In the case of the blend of mangrove and myrab the solubility of the former is much less than that of the latter⁷ and consequently when these two types of tanning materials are blended and extracted, myrab being highly soluble in water is extracted first thus obstructing the mangrove extractives from coming into solution. This would result in more of myrab infusion in the blended extract, which being more of sludge forming materials, results in more sludge in the tan pits. On the other hand, the solubility of crushed babul was found to be slightly less than that of crushed myrab⁷ and hence sludge formation in both these cases did not show much of difference; the blended the leached one giving slightly higher figure than the one leached separately and blended.

References

- 1. Santhanam P.S., Barat S.K., Leather Science 10, 41 (1963)
- 2. Santhanam P.S., Ghosh D., and Nayudamma Y. Leather Science. 14, 179 (1967)
- 3. White T., and Kirby K.S., J.S.L.T.C. 36 148 (1952)
- 3-a. Gustavson K.H. The Chemistry of Tanning Processes, Academic Press, 1956 Page 197.
- 4. Cunningham, G.E. Eade, R., and Ghosh D., Bulletin, CLRI, 9.33 (1962)
- 5. Ghosh D—unpublished result.
- 6. Pollak L., J.A.L.C.A. 29 174, (1934)
- 7. Ghosh D., Thampuran K.R.V., and Balakrishnan, M., The Tanner, 21, 209, (1967).

Acknowledgement

The authors thank Dr. S. K. Barat for his encouragement and guidance in this work. Thanks are due to the authorities of the United States Department of Agriculture for the generous grant under PL-480 programme, which made this work possible. Thanks are also due to the Director, C.L.R.I. for permission to present this paper at this Symposium.

^{*} Paper presented at the ILTA Symposium 1969 at Batanagar.